

Electrostatics of liquid interfaces

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A formalism for the electrostatics of liquid interfaces is proposed based on the surface charge as the source of microscopic electric fields in dielectrics. The surface charge density incorporates the local structure of the interface into electrostatic calculations. The corresponding surface susceptibility and interface dielectric constant provide local closures to the electrostatic boundary value problem. A robust approach to calculate the surface susceptibility from numerical simulations is proposed. The susceptibility can alternatively be extracted from a number of solution experiments, in particular those sensitive to the overall dipole moment of a closed dielectric interface. The theory is applied to the solvent-induced spectral shift and high-frequency dielectric response of solutions.

I. INTRODUCTION

Difficulties with continuum electrostatic models of dielectric interfaces have been recognized in the past,¹ even though not commonly discussed. The present account aims at resolving them for interfaces in liquid dielectrics, where the problems, both conceptual and technical, are particularly difficult and pressing. The discussion starts with the outline of conceptual difficulties of Maxwell's formulation of dielectric polarization.

For a homogeneous dielectric, one commonly starts with the definition of the Maxwell electric field \mathbf{E} in a continuous material made of discrete molecules carrying molecular charges. Those are typically represented by distributed partial charges of atoms and molecular groups. We adopt this convention here and consider the permanent charge distribution and neglect the electronic molecular polarizability. One, therefore, only needs to deal with the changes in positions and orientations of the molecules, leading to fluctuating internal electric fields. These fields are strong and highly non-uniform on the length-scale of individual molecules. The standard approach is to smooth out the variations of the microscopic internal field \mathcal{E} over a "physically small volume" Ω : $\mathbf{E}_p = \langle \mathcal{E} \rangle_\Omega$. The dimensions of the volume Ω need to be small relative to the length-scale of a particular measurement, but large enough to contain many molecules.² The Maxwell field is then defined as the sum of the field \mathbf{E}_0 of external charges and the smoothed-out field of internal charges: $\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_p$. The measurable quantity is actually not the field itself, but its (macroscopic) line integral defining the voltage difference $V = \int \mathbf{E} \cdot d\mathbf{l}$. The standard dielectric experiment measures the material's dielectric constant ϵ as the drop of the voltage in the material compared to vacuum.^{1,3}

How to define the average field \mathbf{E}_p at micro-to-meso length scale has never been adequately resolved. It might appear to have become a straightforward task with the advent of numerical simulations, but exactly how one

should perform the average $\langle \dots \rangle_\Omega$ has never been established. The fields typically reported in the bulk materials by either simulations or by spectroscopy are those produced at a given target molecule by the surrounding condensed phase. It is, however, well established that this local field (which is often identified with the cavity field⁴) is distinct from \mathbf{E} . In fact, the connection between the two fields has been sought by essentially all mean-field theories of dielectrics.^{4,5} Alternatively, following the idea originally advanced by Kelvin for magnetic materials⁶ and by Maxwell for dielectrics,⁷ one can measure the field inside a hollow cavity in the dielectric. However, this approach inevitably requires an interface and the corresponding interfacial polarization when external fields are applied. We address the problem of the field inside a cavity in our discussion below because of its close relation to the general issue of defining fields inside materials, even though the dielectric constant can be defined without invoking cavities.⁸ What needs to be stressed though is that only the voltage difference, local field at a target particle, or a field next to an interface can be measured experimentally.

Introduction of interfaces into dielectrics makes conceptual difficulties more severe. In order to set up the problem, we will consider an interface between vacuum and a dielectric polarized by some external charges indicated by a positive point charge in Fig. 1. We will next consider a part of the interface where there are no external charges, shown by the dashed rectangle in the figure.

The first conceptual problem appears in introducing a dividing surface between dielectrics of different polarity. One can draw a mathematical surface separating the dielectric from a void. This infinitely thin mathematical surface will cut through some surface molecules, remove the corresponding molecular charges, and create the surface charge density^{2,9}

$$\sigma(\mathbf{r}_S) = \mathbf{P}(\mathbf{r}_S) \cdot \hat{\mathbf{n}}. \quad (1)$$

Here, \mathbf{P} is the dipolar polarization density of the dielectric and the normal unit vector $\hat{\mathbf{n}}$ is directed outward to the dielectric; \mathbf{r}_S is the position at the surface. It is immediately clear that the concept of the dividing sur-

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face, and the corresponding surface charge, even though a purely macroscopic construct, requires recognizing the molecular granularity of the material and the separation of charge within the molecule. A surface drawn within the void (dashed line in Fig. 1) will produce zero surface charge and thus will not capture the interfacial polarization by external fields. There is a clear conceptual contradiction between the macroscopic character of the dividing surface and the microscopic distribution of molecular charge and the orientational molecular order at the interface on which the surface charge density must depend.

The exact position of the surface inside the dielectric does not need to be well defined when fields are uniform. In that case, the total dipole between two surfaces of arbitrary shape is zero, and the calculations are not affected by the surface position.¹⁰ This is obviously not true for inhomogeneous fields. This uncertainty is well documented when dielectric cavities need to be defined in solvation models.

Since no external charges are present in the region within the selected area in Fig. 1, the first differential Maxwell equation for the displacement vector \mathbf{D} reads $\nabla \cdot \mathbf{D} = 0$ for any point \mathbf{r} within the region. The displacement vector connects the Maxwell field \mathbf{E} to the dipolar polarization density \mathbf{P} as follows

$$4\pi\mathbf{P} = \mathbf{D} - \mathbf{E}. \quad (2)$$

The displacement vector is transversal ($\nabla \cdot \mathbf{D} = 0$), while the electric field is longitudinal ($\mathbf{E} = -\nabla\Phi$, Φ is the electrostatic potential). Therefore, Eq. (2) represents, according to the Helmholtz theorem,¹ the separation of the polarization field into longitudinal (L) and transverse (T) components.^{11,12}

According to the Helmholtz theorem,^{1,9} any field \mathbf{A} can be split into the longitudinal \mathbf{A}_L and transverse \mathbf{A}_T components such that $\int \mathbf{A}_L \cdot \mathbf{A}_T d\mathbf{r} = 0$. The longitudinal component is

$$\mathbf{A}_L = -\frac{1}{4\pi} \nabla \int \frac{\nabla' \cdot \mathbf{A}'}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (3)$$

where here and below $\mathbf{A}' = \mathbf{A}(\mathbf{r}')$. From this relation one directly gets

$$4\pi\mathbf{P}_L = -\mathbf{E}_p, \quad (4)$$

where $\mathbf{E}_p = -\nabla\Phi_p$,

$$\Phi_p = \int \frac{\rho'_p}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (5)$$

and $\rho_p = -\nabla \cdot \mathbf{P}$ is the polarization charge density. Similarly, since $\nabla \cdot \mathbf{E}_0 = 0$ ($\mathbf{E}_0 = -\nabla\Phi_0$) in the selected region, one gets

$$4\pi\mathbf{P}_T = \mathbf{D} - \mathbf{E}_0. \quad (6)$$

The Maxwell field is then

$$\mathbf{E} = -\nabla\Phi, \quad \Phi = \Phi_0 + \Phi_p. \quad (7)$$

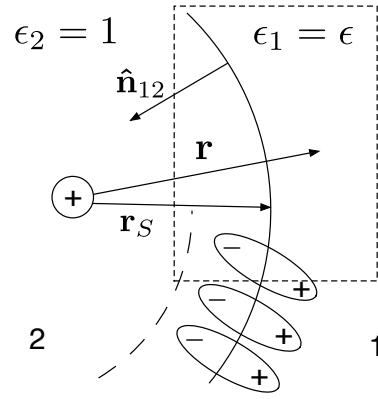


Figure 1. Cartoon of the interface between a dielectric with the dielectric constant ϵ and vacuum. The source of external field is indicated by a positive point charge. The dividing, dielectric-vacuum surface is shown by the solid line. It cuts through surface molecules of the dielectric producing a surface charge density. The latter is sensitive to the choice of the dividing surface since a surface drawn inside the void (long dashed line) produces no surface charge. The area indicated by the dashed rectangle separates a part of the interface with no external charges; $\hat{\mathbf{n}}_{12}$ is the surface normal pointing from medium 1 to medium 2.

Solving differential Maxwell equations requires a constitutive relation connecting \mathbf{D} and \mathbf{E} . For isotropic materials, this is commonly supplied in the form of a simple proportionality involving the macroscopic dielectric constant ϵ , $\mathbf{D} = \epsilon\mathbf{E}$. This relation immediately requires $\nabla \times \mathbf{D} = 0$, which, together with $\nabla \cdot \mathbf{D} = 0$, implies that \mathbf{D} must be a uniform field, equal to zero if boundary conditions at infinity require it. Despite this requirement, the Maxwell constitutive relation is routinely used for problems with spatially varying fields, with the hope that the errors involved are insignificant. The practice of applying Maxwell's equations to polarization of macroscopic dielectrics indeed suggests that they mostly capture the physics of the problem, but extensions to microscopic length-scales have consistently shown complications, both practical and conceptual.

The constitutive relation also implies the proportionality between \mathbf{P} and \mathbf{E} through the susceptibility χ , $\mathbf{P} = \chi\mathbf{E}$, which leads to $\nabla \cdot \mathbf{P} = 0$ and $\nabla \times \mathbf{P} = 0$. This implies $\mathbf{P} = \text{Const}$, $\rho_p = 0$, and $\Phi_p = 0$.

The requirements $\mathbf{D} = \text{Const}$ and $\mathbf{P} = \text{Const}$ are direct consequences of two assumptions: (i) the longitudinal character of \mathbf{E} and the transverse character of \mathbf{D} and (ii) a constitutive relation requiring the proportionality between transverse \mathbf{D} and longitudinal \mathbf{E} and the related proportionality between transverse-longitudinal \mathbf{P} and longitudinal \mathbf{E} . It is the second assumption, that is the constitutive relation, that cannot be generally fulfilled and can be rigorously justified only for uniform fields.¹³ However, the condition of disappearing volume polarization charge ρ_p ($\mathbf{P} = \text{Const}$) can be productively used to formulate a theory relying on the surface charge density for calculating the dielectric response. We next

proceed to re-formulating the problem of electrostatics of liquids starting from the Coulomb law.

II. ELECTROSTATIC BOUNDARY PROBLEM

We start with the microscopic polarization density

$$\mathbf{P}(\mathbf{r}) = \sum_j \langle \mathbf{m}_j \delta(\mathbf{r} - \mathbf{r}_j) \rangle \quad (8)$$

specified by the positions \mathbf{r}_j and orientations of the medium dipoles \mathbf{m}_j ; angular brackets denote an ensemble average. The microscopic electrostatic potential Φ_m directly follows from the dipole-truncated multipolar expansion of the Coulomb law

$$\Phi_m = \Phi_0 + \int \nabla' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \mathbf{P}' d\mathbf{r}'. \quad (9)$$

By using the Gauss theorem, this equation transforms into

$$\Phi_m = \Phi_0 + \Phi_p + \Phi_S, \quad (10)$$

where Φ_p is the scalar potential given by Eq. (5) and the last summand is the potential of the surface charge

$$\Phi_S = \oint \frac{\sigma(\mathbf{r}_S) dS}{|\mathbf{r} - \mathbf{r}_S|}. \quad (11)$$

Note that the surface potential Φ_S does not appear in the standard Maxwell potential in Eq. (7), while it is a necessary consequence of the Coulomb law when interfaces are present. There is of course no dividing surface for a microscopic interface and polarization decays continuously into the void. The surface integral does not appear in Eq. (10) in that case, and we use this consideration below to produce sum rules for the surface charge density $\sigma = \sigma(\mathbf{r}_S)$ [Eq. (1)].

The microscopic electric field $\mathbf{E}_m = -\nabla\Phi_m$ is a non-local property, and that is the fundamental reason for the difficulties with Maxwell's constitutive relations. It is given by the equation

$$\mathbf{E}_m = \mathbf{E}_0 + \int \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{P}' d\mathbf{r}', \quad (12)$$

in which $\mathbf{T}(\mathbf{r} - \mathbf{r}') = -\nabla\nabla' |\mathbf{r} - \mathbf{r}'|^{-1}$ is the long-range dipolar tensor combining both longitudinal and transverse components and thus propagating the corresponding components of \mathbf{P} . The real-space convolution in Eq. (12) is eliminated only in inverted \mathbf{k} -space, where this equation becomes an algebraic relation.

One can next use the Helmholtz theorem [Eq. (3)] to simplify Eq. (12). The result differs inside and outside of the dielectric. Since $4\pi\mathbf{P}_L = -\mathbf{E}_p = 0$ outside the dielectric, the microscopic field becomes

$$\mathbf{E}_m = \mathbf{E}_0 + \mathbf{E}_S, \quad (13)$$

where $\mathbf{E}_S = -\nabla\Phi_S$. When the field is calculated inside the dielectric, a small region around the point of singularity of $\mathbf{T}(\mathbf{r} - \mathbf{r}')$ needs to be taken out,⁹ with the result

$$\mathbf{E}_m = \mathbf{E}_0 - \frac{8\pi}{3}\mathbf{P}_L + \frac{4\pi}{3}\mathbf{P}_T + \mathbf{E}_S. \quad (14)$$

When the Maxwell constitutive relation is used in Eq. (14), one gets

$$\mathbf{E}_m = \frac{\epsilon + 2}{3}\mathbf{E} + \mathbf{E}_S. \quad (15)$$

The first summand here is the Lorentz field,⁵ which is the only term required for \mathbf{E}_m far from interfaces where \mathbf{E}_S vanishes.

Both equations (13) and (14) show that the only non-local part of the microscopic field \mathbf{E}_m caused by the polarized dielectric comes from the field of the surface charges. It is the only field of the polarized dielectric that a measuring device (e.g., a spectroscopic probe) placed either outside of the dielectric or inside a void can directly detect. It is, therefore, this field, and the corresponding surface charge density σ , that is the main focus of our formalism.

The approach we adopt here is to put $\Phi_p = 0$ in Eq. (10), which is equivalent to assuming $\mathbf{P} = \text{Const}$ in the bulk of the dielectric. Here we follow Eyges,^{1,14} who applied this ansatz to dielectrics in general to eliminate contradictions of the standard Maxwell formulation. In this approach, all polarization of the dielectric body contributing to Φ_m is concentrated in the interface, also in agreement with the standard dielectric experiment.

While this approach is just a convenient approximation for dielectrics in general, it provides a correct physical picture for liquid dielectrics. The interfacial dipoles of liquids can nearly freely change their orientation to minimize the surface free energy.¹⁵ Effective screening of the perturbation produced by creating the interface occurs as the result of this structural adjustment, and both the density and orientational perturbations of the liquid propagate only a few molecular layers inside the bulk.^{13,16–20} The polar response is then dominated by the interface and the language of interfacial polarization is the most relevant for describing polarized polar liquids.¹⁷ If, next, microscopic orientational structure of the interface is incorporated into the definition of the surface charge density, one can arrive at a physically motivated formulation of the electrostatics of liquid dielectrics. This is the program of this development, which also attempts to identify experimental observables probing local properties of the interface in order to connect them to the surface charge density.

The potential $\Phi_m \simeq \Phi_0 + \Phi_S$ is created by external and surface charge sources and satisfies the Poisson equation. In order to formulate the boundary conditions, one recalls that the normal component of the field should be discontinuous at the dividing surface, with the discontinuity related to the surface charge density⁹

$$\hat{\mathbf{n}}_{12} \cdot \nabla\Phi_{m1} = \hat{\mathbf{n}}_{12} \cdot \nabla\Phi_{m2} + 4\pi\sigma. \quad (16)$$

Here, $\hat{\mathbf{n}}_{12}$ is the unit normal to the surface directed from region 1 to region 2 and the surface charge density is given as

$$\sigma = (\mathbf{P}_1 - \mathbf{P}_2) \cdot \hat{\mathbf{n}}_{12}. \quad (17)$$

We next proceed to identifying the constitutive relations connecting the surface charge density to the electric field $\mathbf{E}_m = -\nabla\Phi_m$.

III. SURFACE DIPOLAR SUSCEPTIBILITY

The potential of polarized charges Φ_m is a solution of the Poisson equation, satisfying continuity of Φ_m at the dividing surface and the second boundary condition given by Eqs. (16) and (17). The second boundary condition needs to be closed by relating σ to Φ_m or \mathbf{E}_m . This connection is achieved in the plane capacitor dielectric experiment. The electric field inside the capacitor is obviously $E = E_m = 4\pi(\sigma_{\text{ext}} + \sigma)$, where σ_{ext} is the surface charge density at the capacitor's plates. Since the voltage is $V = E_m d$ (d is the thickness of the dielectric), measuring the ratio of capacitance at constant charge with and without the dielectric specifies the susceptibility linking σ to σ_{ext} : $\sigma = \chi\sigma_{\text{ext}}$, $\chi\sigma = \epsilon^{-1} - 1 < 0$. The problem of calculating the potential Φ_p is avoided in this experimental setup by the condition $\mathbf{P} = \text{Const}$ and $\rho_p = 0$.

Following the logic of the plane capacitor calculation, one needs to find the susceptibility connecting σ to \mathbf{E}_0 . This can be achieved by using the linear response theory.^{11,21} To simplify the discussion, we consider the dividing surface separating the dielectric from a void, as in Fig. 1. The interface between two dielectrics follows from subtracting two dielectric/void solutions.

The projection of the polarization density field on the surface normal $\hat{\mathbf{n}}_{12}$ can be calculated in the linear response approximation under the common assumption of a weak external field \mathbf{E}_0

$$\langle P_n \rangle = \beta \int \langle \delta P_n \delta \mathbf{P}'_L \rangle \cdot \mathbf{E}'_0 d\mathbf{r}', \quad (18)$$

where $P_n = \hat{\mathbf{n}}_{12} \cdot \mathbf{P}(\mathbf{r}_S)$, $\beta = 1/(k_B T)$ is the inverse temperature, and the angular brackets denote an ensemble average. Since \mathbf{E}_0 is a longitudinal field, only the longitudinal polarization density \mathbf{P}'_L gives a nonzero contribution to the integral over \mathbf{r}' . The longitudinal and transverse fields mostly fluctuate independently.^{11,22} Therefore, both the surface polarization $\mathbf{P}(\mathbf{r}_S)$ and the correlation function between the polarization fluctuations $\delta \mathbf{P}$ in Eq. (18) refer to their longitudinal projections. For a continuum dielectric $\beta \langle \delta P_{L,\alpha}(\mathbf{r}) \delta P_{L,\beta}(\mathbf{r}') \rangle = \chi_L \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}')$, where $\chi_L = (1 - \epsilon^{-1})/(4\pi)$ is the longitudinal dielectric susceptibility and α, β are the Cartesian components of the vector fields.²³

If the range of the external field variation exceeds the correlation length of the polarization density, the external field can be taken out of the integral in Eq. (18).

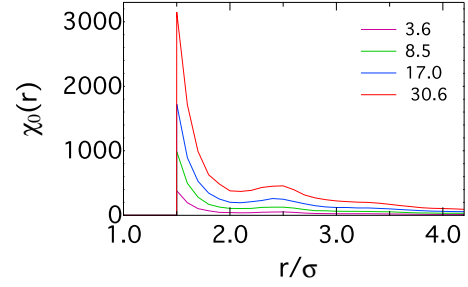


Figure 2. Susceptibility $\chi_0(r)$ from Eq. (21) calculated for spherical concentric layers around the spherical cavity of the radius $R_0/\sigma = 1.0$ in fluids of dipolar hard spheres. The distance from the cavity's center is scaled with the hard-sphere diameter σ . Dielectric constants of dipolar fluids are shown in the legend and the fluids' density is $\rho\sigma^3 = 0.8$.

If one additionally neglects correlations between normal and tangential projections of the polarization density, one gets

$$\langle P_n \rangle = \chi_{0n} E_{0n}, \quad \chi_{0n} = \beta \langle \delta P_n \delta M_{sn} \rangle, \quad (19)$$

where $E_{0n} = \hat{\mathbf{n}}_{12} \cdot \mathbf{E}_0(\mathbf{r}_S)$ and

$$\mathbf{M}_s = \int \mathbf{P}_L(\mathbf{r}) d\mathbf{r} \quad (20)$$

is the total dipole moment of the solvent.

The requirement to use longitudinal fields in Eq. (19) makes this relation largely impractical for the direct analysis of simulations. As is seen from Eqs. (3)–(5) the calculation of the longitudinal projection \mathbf{P}_L from the overall polarization density \mathbf{P} , directly available from simulations, requires convoluting the polarization density of the entire simulation box with the dipolar tensor at each instantaneous configuration. This calculation needs to be repeated for each point \mathbf{r} where the longitudinal polarization density is calculated. Failing to limit the consideration by longitudinal fluctuations incorporates strong transverse polarization fluctuations, which do not couple to the longitudinal electric field and cannot contribute to the susceptibility.

In order to illustrate the extent of error introduced by transverse fluctuations, we show in Fig. 2 the susceptibility calculated from the overall polarization density of a spherical layer, correlated with the total dipole moment \mathbf{M}_s of the simulation cell. The polarization density is calculated for radial layers of the fluid of dipolar hard spheres around a spherical cavity. The corresponding distance-dependent susceptibility is given by the following relation

$$\chi_0(r) = \beta \langle \mathbf{P}(r) \cdot \mathbf{M}_s \rangle. \quad (21)$$

The details of the simulation protocol and the data analysis are given in the Supplementary Material (SM),²⁴ here we discuss only the results.

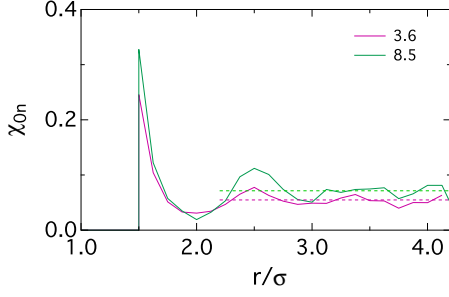


Figure 3. $\chi_{0n}(r)$ from Eq. (22) calculated for concentric layers around a spherical cavity of the radius $R_0/\sigma = 1.0$ in dipolar hard-sphere fluids with dielectric constants indicated in the plot. The dashed lines indicate the results of calculations using a linear fit of the radial correlation functions in Eq. (23) (see text and SM²⁴). All system parameters are the same as in Fig. 2.

The susceptibility $\chi_0(r)$ spikes to very high values near the interface, then slowly decays to the bulk. Qualitatively similar results have been reported for aqueous interfaces.^{19,25,26} On the other hand, the longitudinal symmetry of the polarization field, which makes direct calculations according to Eq. (19) largely impractical, can be used to obtain an equation more suitable for numerical applications. By applying Eqs. (4) and (5) one can re-write Eq. (18) as follows

$$\langle P_n \rangle = \beta \sum_i q_i \langle \delta P_n \delta \Phi_{p,i} \rangle, \quad (22)$$

where the sum is over the external charges q_i and fluctuations $\delta \Phi_{p,i}$ of the solvent potential at those charges. Figure 3 illustrates the application of this formula when one probe charge is placed at the center of the spherical cavity carved from the fluid of dipolar hard spheres. The susceptibility is calculated for concentric shells of radius r around the cavity and thus becomes a function of r . As is seen, eliminating the transverse fluctuations from $\chi_0(r)$ in Eq. (22) significantly reduces the susceptibility. It still preserves its spike at the distance of the closest approach of the solvent to the cavity and oscillations decaying into the bulk.

The uncertainty with the choice of the interfacial susceptibility χ_{0n} from the distance-dependent, and oscillatory, function $\chi_{0n}(r)$ can be resolved by calculating the integrated radial dipole moment of the hydration layer within the r -shell: $M(r) = \sum_{r_j < r} \mathbf{m}_j \cdot \hat{\mathbf{r}}_j$, $\hat{\mathbf{r}}_j = \mathbf{r}_j/r_j$. For a charge placed at the center of the cavity one gets

$$\chi_{0n}(r) = (\beta/4\pi) \frac{d}{dr} \langle \delta M(r) \delta \Phi_p(0) \rangle, \quad (23)$$

where $\Phi_p(0)$ is the solvent potential at the center of the cavity. As is shown in the SM,²⁴ $\langle \delta M(r) \delta \Phi_p(0) \rangle$ is well represented by a linear function of r , thus producing a

constant χ_{0n} for the derivative in Eq. (23). The results of these calculations are shown by the dashed lines in Fig. 3, confirming that taking the derivative in Eq. (23) is consistent with averaging the oscillations of $\chi_{0n}(r)$ out. We turn to the polarity of the interface below again, but first discuss the closure of the boundary value problem in Eqs. (16) and (17) in terms of the electrostatic potential Φ_m and define the dielectric constant of the interface.

We will use the plane capacitor geometry to establish the connection between χ_{0n} and the susceptibility to the overall field $\langle P_n \rangle = \chi_n E_n$, $E_n = \hat{\mathbf{n}}_{12} \cdot \mathbf{E}_m(\mathbf{r}_S)$. For the plane capacitor, $E_n = E_{0n} - 4\pi \langle P_n \rangle$ (note the convention for the surface normal), and one gets

$$\chi_n = \chi_{0n} / (1 - 4\pi \chi_{0n}). \quad (24)$$

The second boundary condition can now be re-written in the form commonly accepted in the theories of dielectrics

$$\tilde{\epsilon}_1 \hat{\mathbf{n}}_{12} \cdot \nabla \Phi_{m1} = \tilde{\epsilon}_2 \hat{\mathbf{n}}_{12} \cdot \nabla \Phi_{m2}, \quad (25)$$

where

$$\tilde{\epsilon}_i = 1 + 4\pi \chi_{n,i} = (1 - 4\pi \chi_{0n,i})^{-1}. \quad (26)$$

Spontaneous polarization is possible when dipole and quadrupole moments of the liquid compete to minimize their free energy in the interface.¹⁵ This effect is particularly strong for water,²⁰ where the competition is between an axial dipole and a mostly non-axial quadrupole. In such cases, a non-zero surface charge density exists even at zero fields and $\sigma = \sigma_s + \chi_n E_n$. Equation (25) then modifies to

$$\tilde{\epsilon}_1 \hat{\mathbf{n}}_{12} \cdot \nabla \Phi_{m1} = \tilde{\epsilon}_2 \hat{\mathbf{n}}_{12} \cdot \nabla \Phi_{m2} + 4\pi \sigma_s. \quad (27)$$

In addition to a non-zero offset of the surface charge density, one can also anticipate a possibility of χ_n depending on the sign of E_n to reflect the well-established asymmetry of the water's linear response to ions of opposite charge.^{27,28}

The equations for the potential Φ_m are the same as Maxwell's equations and, therefore, standard numerical Poisson equation solvers can be used. Similarly to the Maxwell formulation, the theory requires only one susceptibility parameter. On the other hand, even though Eq. (27) casts the problem of interfacial electrostatics in the familiar terms of the boundary value problem, the knowledge of the susceptibility χ_{0n} responding to the field of external charges is sufficient for the direct calculation of the electrostatic potential Φ_m from the known distribution of external charges and the corresponding electric field \mathbf{E}_0 . Although we cannot prove it here, the connection between χ_n and χ_{0n} given by Eq. (24) might be nonuniversal. The formulation in terms of \mathbf{E}_0 and χ_{0n} is preferable from this perspective.

The "interface dielectric constant" $\tilde{\epsilon}_i$ in Eqs. (26) and (27) will in most cases of interest be distinct from the standard dielectric constant supplied by the dielectric

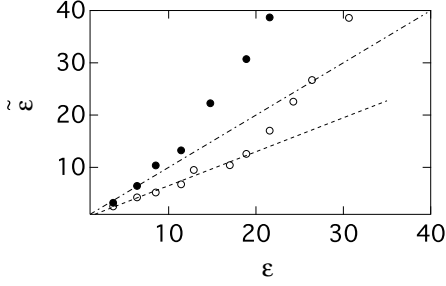


Figure 4. $\tilde{\epsilon}$ calculated from Eqs. (26) and (23) vs. the bulk ϵ of fluids of dipolar hard spheres. The points are the simulation results for the cavity radius $R_0/\sigma = 1.0$ (closed circles) and $R_0/\sigma = 3.0$ (open circles). The dashe-dotted line marks $\tilde{\epsilon} = \epsilon$ to guide the eye. The dashed line with the slope 0.65 is a linear regression through seven lowest polarity points shown by the open circles.

experiment, which is specified by the “tilde” sign. However, for the dielectric polarization in a plane capacitor we get $\tilde{\epsilon} = \epsilon$ and the standard longitudinal susceptibility $\chi_{0n} = \chi_L = (1 - \epsilon^{-1})/(4\pi)$. Therefore, for a plane capacitor, $\tilde{\epsilon}$ yields the enhancement of the capacitance reported experimentally as the dielectric constant of the material. This agreement is not expected to hold for more complex interfacial geometries and nonuniform external fields, as we now show for the problem of spherical cavities in fluids of dipolar hard spheres.

The dielectric constants of the interface $\tilde{\epsilon}$, obtained by substituting constant-value susceptibilities χ_{0n} from Eq. (23) to Eq. (26), are in fair agreement with the dielectric constants of the bulk for relatively small cavities. In the case of $R_0/\sigma = 1.0$ (closed circles in Fig. 4), $\tilde{\epsilon}$ is very close to ϵ for weakly polar fluids, and then shows an upward increase compared to the bulk for more polar liquids. A similar trend is seen for a larger cavity ($R_0/\sigma = 3.0$, open circles in Fig. 4), but in that case the polarity of the interface starts from values lower than the polarity of the bulk. This latter outcome is consistent with the emergence of a new scaling, with the cavity size, of the average cavity potential once the cavity is grown above a critical radius.¹⁷ We now turn to this subject and the related formulation of sum rules for the surface charge density.

The free energy of polarizing the dielectric can be written in terms of the polarization charges as follows²

$$\Delta F = \frac{1}{2} \int \sigma \Phi_0 dS + \frac{1}{2} \int \rho_p \Phi_0 d\mathbf{r}. \quad (28)$$

In the current model, $\rho_p = 0$ and only the first integral appears in the free energy. On the contrary, for a microscopic interface, there is no dividing surface and only the second integral contributes. Since the polarization free energy should not depend on the model, one can use this condition to formulate the sum rule for σ . By applying

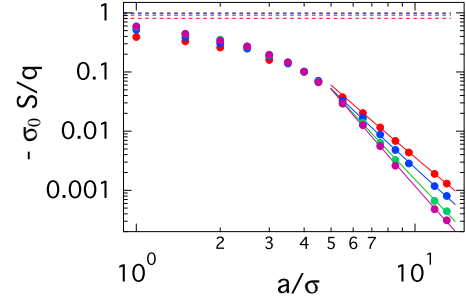


Figure 5. $-\sigma_0 S/q$ vs. $a/\sigma = R_0/\sigma + 1/2$ for cavities in dipolar hard spheres with $\epsilon = 3.6$ (red), 8.5 (blue), 30.6 (green), and 93.7 (magenta); R_0 is the radius of the hard-sphere cavity and $R_0 + \sigma/2$ is the distance of the closest approach of the solvent. The solid lines are linear fits to large cavity portions of the data. The regression slopes are: -3.8 (red), -4.1 (blue), -4.7 (green), and -5.1 (magenta). The dashed lines indicate the results of Eq. (31).

Eq. (4), we can write this condition in the form

$$\int \sigma \Phi_0 dS = \sum q_i \Phi_{p,i}, \quad (29)$$

where, as in Eq. (22) above, q_i are the external charges producing the external potential Φ_0 ; $\Phi_{p,i}$ are the potentials of the polarized solvent at the positions of these charges. In the specific case of a single ion at the center of a spherical void of radius a one gets

$$\Phi_p(0) = 4\pi a \sigma_0 = -4\pi a P_r|_{r=r_S}, \quad (30)$$

where P_r is the radial projection of the average polarization density and σ_0 is the angular-averaged surface charge density ($\ell = 0$ expansion term in Eq. (33) below). The potential $\Phi_p(0)$ at the void’s center adds to the potential difference at the planar liquid-air interface to make the electrochemical potential measuring the work of transferring an ion from the gas phase into its cavity inside the liquid.^{20,29,30}

We illustrate the application of the sum rules in Eq. (29) to numerical simulations of cavities in dipolar fluids.¹⁷ We consider polarization of the dielectric by an ion with charge q placed at the center of the cavity of radius a . Dielectric models suggest that the product of the surface charge density with the surface area $S = 4\pi a^2$ remains constant

$$-q^{-1} \sigma_0 S = 1 - \epsilon^{-1}, \quad (31)$$

This relation, used in the sum rule in Eq. (30), yields $\Phi_p(0) = -(1 - \epsilon^{-1})(q/a)$ and the corresponding Born solvation free energy $(q/2)\Phi_p(0)$.

The potential $\Phi_p(0)$ can be extracted from simulations of cavities in liquids by the use of the linear response approximation,²¹ which suggests that the average potential of the solvent in response to the charge can be obtained from the variance of the potential fluctuations in

the absence of the charge.¹⁷ One then gets

$$-q^{-1}\sigma_0 S = (\beta a/2)\langle(\delta\Phi_p(0))^2\rangle. \quad (32)$$

The results of MC simulations¹⁷ for three fluids of dipolar hard spheres surrounding cavities of varying radius are shown in Fig. 5. The points are the simulation results plotted against the cavity size. They are compared to the predictions of Eq. (31) shown by the dashed lines.

The results presented in Fig. 5 illustrate why the focus on the interfacial properties is required for a physically motivated model of liquid electrostatics. As the size of the cavity grows, the orientational structure of the interface changes, thus altering the corresponding surface charge density and the cavity potential related to it. As a result of these structural changes, the invariance of $\sigma_0 S$ suggested by Eq. (31) does not hold anymore. A new scaling $\sigma_0 S \propto a^{-\alpha}$, $\alpha \simeq 4 - 5$ emerges, which is not anticipated by the standard electrostatic arguments. With this new scaling, the solvent response $\Phi_p(0)$ to a charge inside a void scales down faster than a^{-1} for voids larger than the critical size approximately four times the size the solvent molecule. The direct physical consequence of this result is that large solutes, with internal charges effectively screened by this new scaling, require surface charges and corresponding surface solvation³¹ to build up the solvation stabilization energy sufficient for solubility.

IV. POLARIZED CAVITY IN A UNIFORM ELECTRIC FIELD

Here we illustrate the new boundary conditions for the electrostatics of liquids by applying them to the problem of a spherical void polarized by a uniform external field (Fig. 6). This problem directly applies to the high-frequency dielectric response of solutions³² and to optical spectroscopy as we discuss below.

In order to come up with specific parameters of the void's interface, we will use the axial symmetry of the problem and expand σ in Legendre polynomials $P_\ell(\cos \theta_0)$ of the polar angle θ_0 between the z -axis aligned with the external field and the position \mathbf{r}_S at the dividing spherical surface (Fig. 6)

$$\sigma(\theta_0) = \sum_{\ell} \sigma_{\ell} P_{\ell}(\cos \theta_0). \quad (33)$$

It is easy to see that expansion terms of order ℓ are connected to the z -components of surface multipoles of the corresponding order. One gets the z -projection of the interfacial dipole $M_{0z}^{\text{int}} = \sigma_1 \Omega_0$ at $\ell = 1$ and zz -projection $Q_{0,zz}^{\text{int}} = (3/5)\sigma_2 a \Omega_0$ of the surface quadrupole at $\ell = 2$; Ω_0 is the void's volume.

The potential Φ_m (see SM²⁴) is the solution of the Poisson equation for a spherical cavity polarized by a uniform external electric field such that the local field \mathbf{E}_m becomes the Maxwell field \mathbf{E} in the bulk of the polarized

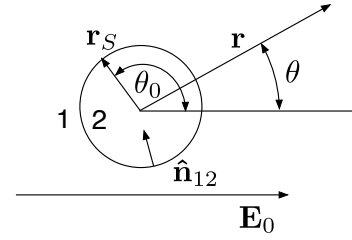


Figure 6. Spherical cavity polarized by the field of external charges \mathbf{E}_0 .

dielectric. From this solution, the local electrostatic field at the void's center is

$$E_{m,z}(0) = E - (4\pi/3)\sigma_1. \quad (34)$$

The field at the center of the cavity is fully defined by the interface dipole, or the σ_1 projection of the surface charge density.

One can make one step further to connect σ_1 to χ_n . The field E_n at the cavity's surface (SM²⁴), is related, through χ_n , to the surface charge density given by Eq. (33). By equating the $\ell = 1$ components in the two equations, one gets the desired relation

$$\sigma_1 = -\frac{\chi_n E}{1 + (8\pi/3)\chi_n} = -\frac{\chi_{0n} E}{1 - (4\pi/3)\chi_{0n}}. \quad (35)$$

In terms of the local dielectric constant $\tilde{\epsilon}$ in Eq. (26), this relation becomes

$$\sigma_1 = -\frac{3}{4\pi} \frac{\tilde{\epsilon} - 1}{2\tilde{\epsilon} + 1} E. \quad (36)$$

The second term in this equation is easily recognized as the dielectric reaction field response appearing in theories dielectrics;^{4,5} $E_{m,z}(0)$ in Eq. (34) then becomes the corresponding expression for the cavity field.⁵ If one assumes $\tilde{\epsilon} = \epsilon$, one arrives at the Maxwell result for the dipole moment induced at a spherical void by a uniform external field⁹

$$M_{0z}^{\text{int}} = -\frac{3\Omega_0 P}{2\epsilon + 1}, \quad (37)$$

where $P = (4\pi)^{-1}(\epsilon - 1)E$ is the dielectric polarization far away from the interface.

These calculations illustrate that the results of Maxwell's electrostatics are a part of the proposed formalism. However, the polarization of the interface of a polar liquid facing a void deviates significantly from the predictions of Maxwell's electrostatics due to anisotropic orientational structure of the interfacial dipoles, implying that Eq. (37) does not agree with simulations,³³ or, alternatively, $\tilde{\epsilon} \neq \epsilon$. The current formulation provides more flexibility to account for such results by connecting electrostatic calculations to experiments reporting local interfacial properties, such as interfacial multipolar moments.

V. CONNECTION TO EXPERIMENT

Electrostatic fields in condensed media are traditionally quantified by the solvent induced shift of optical³⁴ or vibrational³⁵ transition lines. The electrostatic component of the shift, often dominant,³⁶ is given by the product of the dipole moment change of the chromophore Δm and the reaction field R in the ground state in equilibrium with the ground-state dipole m_g

$$h\Delta\nu = -\Delta m R. \quad (38)$$

From derivations presented above, $R = -(4\pi/3)\sigma_1$, but the interface dipole, represented by σ_1 , now needs to be updated with the account for the polarizing field of the central dipole of the chromophore m_g . Repeating the steps leading to Eq. (36), we obtain

$$\sigma_1 = -\frac{2m_g}{a^3} \frac{\chi_n}{1 + (8\pi/3)\chi_n}. \quad (39)$$

From this relation, the reaction field becomes

$$R = \frac{m_g}{a^3} \frac{(8\pi/3)\chi_n}{1 + (8\pi/3)\chi_n} = \frac{2m_g}{a^3} \frac{\tilde{\epsilon} - 1}{2\tilde{\epsilon} + 1}. \quad (40)$$

One recovers the standard Onsager relation⁴ for $R(\epsilon)$ when $\tilde{\epsilon} = \epsilon$. Note that $R(\epsilon) - R(\epsilon_\infty)$ is often used in Eq. (38) to separate the response due to the high-frequency dielectric constant ϵ_∞ from the total polar response $R(\epsilon)$. This is not required in Eq. (40) since χ_n can be understood as the permanent dipole susceptibility of the interface. This susceptibility can, therefore, be tabulated by spectroscopic shifts of dipolar dyes.³⁶ The same function can be extracted from high-frequency dielectric measurements of solutions as we discuss next.

When the frequency of the capacitor field or of radiation exceeds the characteristic relaxation frequency of the solute dipole, the solution response approaches that of the solution of voids. The measurement of the absorption coefficient or the dielectric constant of the solution gives access to the dipolar susceptibility of the cavities produced by the excluded solute volumes in the solvent, $\chi_1 = \sigma_1/E$.³² The solution dielectric constant ϵ_{sol} can be found from the equation³²

$$(\epsilon/\epsilon_{\text{sol}}) = 1 + \eta_0(\epsilon - 1) [1 + (8\pi/3)\chi_1] \quad (41)$$

in which η_0 is the solute volume fraction

The slope of the dielectric decrement $\Delta\epsilon = \epsilon_{\text{sol}} - \epsilon$ vs. η_0 gives access to the susceptibility χ_1 and, through Eq. (35), to χ_n . Experimental absorption data for aqueous solutions show that the slope, and χ_1 extracted from it, change significantly depending on the nature of the solute and the corresponding interfacial structure of water.³⁷ Dielectric constant obviously does not capture these variations. Therefore, measurements of solution absorption can potentially replace the dielectric experiment in providing the local interface susceptibility.

Equations (38), (40), and (41) suggest that high-frequency dielectric and spectroscopic measurements give access to the same interface susceptibility. One can, therefore, combine these equations into a relation including only experimentally accessible properties of solutions

$$(\epsilon/\epsilon_{\text{sol}}) = 1 + \eta_0(\epsilon - 1) [1 + h\Delta\nu a^3/(\Delta m m_g)]. \quad (42)$$

Measurements of the mobility of particles suspended in a liquid³⁸ provide access to the quadrupole moment of the interface $Q_{0,zz}^{\text{int}} = (3/5)\sigma_2 a \Omega_0$ arising from a non-zero second-order term in Eq. (33).³⁹ The anisotropic orientational structure of the interface creates conditions for an anisotropic response to the applied field. The difference in response implies different local electric field E_m on the opposite sides of the suspended particle and, correspondingly, different electrostatic energy densities. This condition implies a gradient of the chemical potential projected on a dragging force acting on the suspended particle. The force along the external field applied to a particle carrying the charge q becomes

$$F_z = (q + 2Q_{0,zz}^{\text{int}}/a^2) E. \quad (43)$$

Measuring the force, or electrophoretic mobility, provides experimental access to the quadrupole moment of a closed interface.

VI. CONCLUSIONS

The Maxwell constitutive relations $\mathbf{D} \propto \mathbf{E}$, $\mathbf{P} \propto \mathbf{E}$ establish simple proportionality rules between fields of different symmetry. The longitudinal and transverse components of the polarization density field \mathbf{P} , mixed in the Maxwell constitutive relations, carry distinctly different physical properties.¹² The distinction is reflected by the $k \rightarrow 0$ behavior of their corresponding structure factors:²³ nearly flat for the longitudinal projection and strongly peaked, and infinitely increasing at the ferroelectric transition, for the transverse projection.²² Since continuum electrostatics is recovered in the $k \rightarrow 0$ limit of k -dependent dipolar response functions,⁴⁰ there is a good physical reason for the linear constitutive relations to be successful for the longitudinal projection, but they are expected to fail for the transverse projection.

The enormous simplification provided by the constitutive relations is the ability to cast the problem in terms of the Poisson equation with a single susceptibility (dielectric constant) entering the boundary conditions.⁹ This procedure presents some clear conceptual difficulties, but, from the practical perspective, has also run into problems when applied to molecular-size objects^{22,41} and to nanometer-scale liquid interfaces.^{17,33} The deviations from the expected behavior are not limited to quantitative disagreements in calculated electrostatic energies, but reach the level of qualitative differences. The scaling of the liquid polar response to an ion placed in the center of a void¹⁷ shows a cross-over from the expected $\propto a^{-1}$

scaling (Born model) to $\propto a^{-(4-6)}$ scaling with increasing void's radius a (Fig. 5). In addition, the electric field inside a void carved from a uniformly polarized dielectric does not reach the value $\simeq (3/2)E$ at $\epsilon \gg 1$,^{4,5} but instead shows the behavior consistent with the Lorentz formula for the cavity field $\simeq (\epsilon/3)E$.^{22,33}

These effects, and potentially a number of others, are different manifestations of the same physical phenomenon: the localization of the polar response in the liquid's interfacial layer, instead of its spreading through the dielectric, as anticipated by the Maxwell picture.¹³ For the localized interfacial response, the specific orientational structure of the interfacial multipoles strongly affects the electrostatic potential and field produced by the interface. The electrostatic problem can then be recast in terms of the interface-specific surface charge density.

An approach consistent with the picture of surface polarization dominating the electrostatic response of a liquid dielectric^{17,22,33} is proposed here. It reformulates the boundary value electrostatic problem in terms of the surface charge density and the corresponding surface charge susceptibility. Importantly, the local surface susceptibility is introduced for the longitudinal component of the polarization field only, thus avoiding transverse polarization fluctuations strongly enhancing the susceptibility, but decoupled from the longitudinal external field. This formalism offers a robust route to the calculation of the dielectric constant of the interface.

The interface susceptibility characterizes specific interfaces and aims to replace the dielectric constant as the input into the electrostatic boundary value problem. It can be calculated from polarization correlation functions supplied by numerical simulations or related to experimental observables. In particular, the dipole moment of the interface (the first multipole of the surface charge density) enters a number of observables characterizing solutions polarized by long-wavelength stationary or oscillatory (e.g., radiation) fields.

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